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(54) **LEATHER COATED WITH FLUORORESIN**

(57) To provide a coated leather being excellent in stain removability and solvent resistance and having cold resistance and flexing fatigue resistance equal to those of conventional urethane resin coating. A coating

film obtained by curing a fluorine-containing resin coating composition comprising a fluorine-containing resin having a reactive curable group and a curing agent is formed as an outermost layer directly on the leather or through a primer layer.

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**Description****TECHNICAL FIELD**

5 [0001] The present invention relates to a leather coated with a fluorine-containing resin being excellent in stain-proofing property (stain-removability) and solvent resistance, a production method thereof and a leather product produced by using the coated leather.

**BACKGROUND ART**

10 [0002] There are various methods of finishing a surface of a leather depending on kind of a raw leather and application of leather products. Except un-finished leathers such as fur, suede and nubuck, a resin coating film is formed on a surface of a leather for finishing. The resin coating film is formed for protection of a leather surface and for a good appearance thereof and in addition, for preventing a stain from soaking into a leather and for easily wiping off sweat and stain.

15 [0003] As a material for coating on a surface of a leather, non-fluorine-containing materials such as urethane resins, nitrocellulose lacquer, proteins such as casein, and higher fatty acid ester wax are used. Among them, urethane resins are excellent in adhesion, flexibility, transparency, bending resistance, cold resistance, chemical resistance, heat resistance and abrasion resistance and are widely used.

20 [0004] However conventional coating films are hydrophilic or hydrophobic. In case of the former hydrophilic film, aqueous stains such as mud and soy sauce easily adheres thereto, and in case of the latter hydrophobic film, oily stains such as sebaceous matter, rouge and ink of ball-point pen easily adheres. Those stains are difficult to be removed by wiping, etc. For the same reason, solvent resistance is also not sufficient.

25 [0005] On the other hand, while a fluorine-containing resin coating film is excellent in water- and oil-repellency and solvent resistance, it is inferior generally in flexibility and poor in adhesion to a leather surface or a primer coating film. Therefore it has been considered that the fluorine-containing resin coating film is not practical as a coating film for a leather which is demanded to have a high flexibility.

30 [0006] An object of the present invention is to provide a leather material and leather product having improved stain-proofing property, (stain removability) and solvent resistance while making the best use of feeling of the leather product and maintaining required properties, for example, flexibility, cold resistance and bending resistance.

[0007] The inventors of the present invention have made studies with respect to the fluorine-containing resin coating film which has been considered impractical and as a result of trial and error, have found that when the fluorine-containing resin coating film having a reactive curable group is used, the above-mentioned objects are attained and stain-proofing property and solvent resistance which have not been obtained before can be imparted to a leather.

**DISCLOSURE OF INVENTION**

35 [0008] Namely the present invention relates to a leather coated with a fluorine-containing resin which has a fluorine-containing coating film as an outermost layer formed on a surface thereof, in which in stain removing test according to JIS L 0805, a grey scale is grade 4 or more and in ethanol resistance test according to JIS K 6547 by using a clock meter type friction tester, an area of chipped-off fluorine-containing coating film is 50 % or less.

40 [0009] In the preferred leather of the present invention, cracking does not arise on the fluorine-containing coating film in a cold resistance test in which the coated leather is allowed to stand at -5°C for 24 hours and then folded with a coated surface being faced outward, and also cracking does not arise on the fluorine-containing coating film when the coated leather is folded 30,000 times by using a flexometer described in JIS K 6545.

45 [0010] It is preferable that a weight of the fluorine-containing resin coating film is not less than 2 g/m<sup>2</sup>.

[0011] Each test used herein is carried out by the following methods and the results thereof are evaluated as follows.

**(1) Stain removing test**

50 [0012] A coating composition to be tested is coated in a specified amount on a white cowhide (having a urethane resin coating film of 10 g/m<sup>2</sup> as a primer layer) by using a spray gun (a small size spray gun W-88 available from ANEST IWATA CORPORATION) and cured at 50°C for two minutes to give a coated leather. To the coated leather is applied staining substances mentioned hereinafter, followed by allowing to stand for 30 minutes. Then the stain adhered on the coated leather is wiped softly five times with a cotton cloth impregnated with a commercially available stain removing agent mentioned hereinafter. A floating stain is wiped off sufficiently with a cotton cloth which is not impregnated with a stain removing agent. Then a state of stain remaining on the leather surface is compared (with naked eyes) to a grey scale for staining of JIS L 0805.

[0013] The grey scale for staining of JIS L 0805 is classified into nine grades, namely from grade "1" of the most stained degree through "1-2", "2", "2-3", "3", "3-4", "4", "4-5" up to "5" of the most stainless degree for evaluation of staining degree.

5 Staining substance

Kind of stain

[0014]

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Rouge: "CALIFORNIA COLORS No. 4" available from NIHON KOLMAR CO., LTD.

Mustard: Mustard for hot dog available from Q.P. CORPORATION

Ball-point pen: Oil ink ball-point pen (black) SOFT STAINLESS SA-S available from MITSUBISHI PENCIL CO., LTD.

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Stain removing agent

[0015]

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Detergent: Diluted aqueous solution of 30 % by weight of neutral synthetic detergent "MAMA ROYAL NATUR" available from LION CORPORATION

Cleaner for leather: "MERCY CLEANER" available from SANETCHI K.K.

(2) Ethanol resistance test

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[0016] A coating composition to be tested is coated in a specified amount on a dark blue cowhide (having a urethane resin coating film of 20 g/m<sup>2</sup> as a primer layer) by using a spray gun (the same one as used in the stain removing test) and cured at 50°C for two minutes to give a coated leather. Some drops of an aqueous solution of 75 % by weight of ethanol are put on a surface of the coated leather, and after allowing to stand for three minutes, are soaked up with a paper. Immediately after that, the leather surface where the droplets of ethanol has been put is rubbed with a dry white cotton cloth five times by using a clock meter type friction tester described in JIS K 6547, and an area percentage of coating film chipped off is evaluated with naked eyes.

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(3) Cold resistance test

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[0017] A coated white cowhide produced in the same manner as in the above-mentioned stain removing test is kept in a refrigerator of -5°C for 24 hours. Immediately after taken out, the coated leather is folded with the coated surface being faced outward. In the folded state, a red aqueous ink is applied to the folded part and immediately wiped off softly and unfolded. Cracking on the coating film is evaluated with naked eyes (if there is a cracking, it appears by a red line).

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(4) Flexing fatigue resistance test

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[0018] After a coated white cowhide produced in the same manner as in the above-mentioned stain removing test is bent 30,000 times by using a flexometer described in JIS K 6545, a red aqueous ink is applied to the bent part and immediately wiped off. Then cracking on the coating film is evaluated with naked eyes (if there is a cracking, it appears by a red line).

[0019] The leather coated with a fluorine-containing resin of the present invention can be produced by applying a curable fluorine-containing resin coating composition comprising a fluorine-containing resin having a reactive curable group and a curing agent to a leather directly or through a primer layer and then curing a coating film.

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[0020] Example of the preferred reactive curable group of the fluorine-containing resin having the curable reactive group (hereinafter referred to as "curable fluorine-containing resin") is at least one of hydroxyl group, amino group, epoxy group, carboxyl group, mercapto group, hydrolyzable silyl group, amido bond, urethane bond and urea bond. Particularly preferred is hydroxyl group. It is preferable that a hydroxyl value of a fluorine-containing resin having hydroxyl group is not more than 200 mgKOH/g.

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[0021] Preferable examples of a trunk chain of the curable fluorine-containing resin are polymers having at least one of a recurring unit of chlorotrifluoroethylene unit, tetrafluoroethylene unit, trifluoroethylene unit, hexafluoropropylene unit, vinylidene fluoride unit and vinyl fluoride unit.

[0022] Examples of the curing agent to be used are an isocyanate compound, amino resin, acid anhydrides, polysilane compounds, polyepoxy compounds and silane compounds having isocyanate group.

[0023] As mentioned above, the fluorine-containing resin coating film may be formed on a leather surface directly or through a primer layer. When the coating film is formed through a primer layer, it is preferable to use, as a material for the primer layer, an acrylic resin, methacrylic resin, urethane resin, acrylonitrile resin, butadiene resin, styrene resin, vinyl chloride resin, vinylidene chloride resin, vinyl acetate resin or a mixture of two or more thereof.

[0024] Further the present invention relates to various leather products having the above-mentioned leather coated with a fluorine-containing resin, for example, interior goods for vehicle and building, furniture, shoes, bags, clothes, small leather articles, etc.

#### BEST MODE FOR CARRYING OUT THE INVENTION

[0025] The fluorine-containing resin coating film formed as the outermost layer of the leather coated with the fluorine-containing resin coating composition of the present invention can be obtained by applying the curable fluorine-containing resin coating composition comprising a curable fluorine-containing resin having a reactive curable group and a curing agent to a leather and then curing it.

[0026] Examples of the reactive curable group of the curable fluorine-containing resin are, as mentioned above, hydroxyl group, amino group, epoxy group, carboxyl group, mercapto group, hydrolyzable silyl group (for example, trimethoxysilyl group, triethoxysilyl group, etc.) amido bond, urethane bond and urea bond. Particularly hydroxyl group is preferred from the viewpoint of stability of the resin and curing reactivity. It is preferable from the viewpoint of feeling of a coated leather and flexing resistance that hydroxyl group is introduced so that a hydroxyl value is not more than 200 mgKOH/g.

[0027] For example, concretely there are curable fluorine-containing resins described in JP-B-60-21686, JP-A-3-121107, JP-A-4-279612, JP-A-4-28707, JP-A-2-232221, etc. With respect to a molecular weight, it is preferable from the viewpoint of curability and workability at coating work that a number average molecular weight (measured with GPC) is from 1,000 to 500,000, particularly 1,500 to 100,000.

[0028] The curable fluorine-containing resins are those containing chlorotrifluoroethylene (CTFE) unit, tetrafluoroethylene (TFE) unit, trifluoroethylene (TrFE) unit, hexafluoropropylene (HFP) unit, vinylidene fluoride (VDF) unit or vinyl fluoride (VF) unit preferably in an amount of not less than 20 % by mole. Particularly curable fluorine-containing resins containing in an amount of 20 to 60 % by mole are preferred from the viewpoint of stain-proofing property and solubility in a solvent.

[0029] Examples of the usable curable fluorine-containing resin commercially available are, for instance, organic solvent type fluorine-containing resin coating compositions such as ZEFFLE GK (trade name) series available from DAIKIN INDUSTRIES, LTD., LUMIFLON (trade name) series available from ASAHI GLASS CO., LTD., CEFRAL COAT (trade name) available from CENTRAL GLASS CO., LTD., FLUONATE (trade name) series available from DAINIPPON INK AND CHEMICALS, LTD., and ZAFLOX (trade name) series available from TOAGOSEI CO., LTD.

[0030] The curable fluorine-containing resin may be blended with other resins, for example, one or two or more of a styrene resin, (meth)acrylic resin, polyester resin, alkyd resin, melamine/formaldehyde resin, polyisocyanate resin, epoxy resin, vinyl chloride resin (for example, vinyl chloride/vinyl acetate copolymer, etc.), ketone resin, petroleum resin, chlorinated polyolefins such as chlorinated polyethylene and chlorinated polypropylene, inorganic resins such as silica gel and silicate, fluorine-containing resins other than the above-mentioned curable fluorine-containing resins of the present invention (for example, homopolymers of tetrafluoroethylene and chlorotrifluoroethylene and copolymers thereof with other monomer), and the like. The other resins are not limited to them.

[0031] The curing agent which is used in the present invention as another component of the curable fluorine-containing resin coating composition may be one which reacts with the above-mentioned reactive curable group for curing of the fluorine-containing resin. For example, isocyanate compounds, amino resins, acid anhydrides, polysilane compounds, polyepoxy compounds, isocyanate group-containing silane compounds, and the like are used usually.

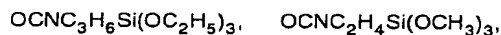
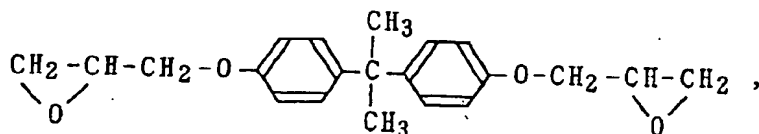
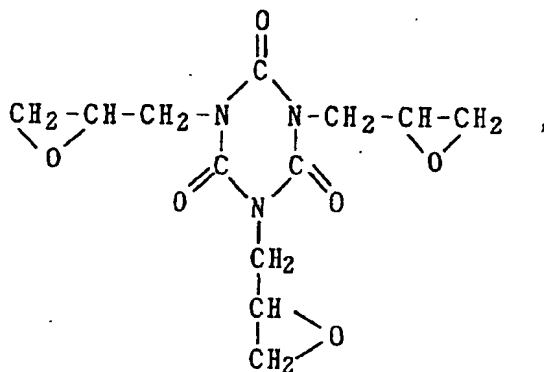
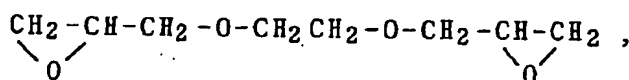
[0032] Non-restricted examples of the isocyanate compound are, for instance, 2,4-tolylene diisocyanate, diphenylmethane-4,4'-diisocyanate, xylylene diisocyanate, isophorone diisocyanate, lysine methyl ester diisocyanate, methylcyclohexyl diisocyanate, trimethylhexamethylene diisocyanate, hexamethylene diisocyanate, n-pentane-1,4-diisocyanate, termonomers thereof, adducts and biurets thereof, polymers thereof having two or more isocyanate groups and blocked isocyanates.

[0033] Non-restricted examples of the above-mentioned amino resin are, for instance, urea resin, melamine resin, benzoguanamine resin, glycoluril resin, methylolated melamine resin obtained by methylolating melamine, alkyl-etherified melamine resins obtained by etherifying methylolated melamine with alcohol such as methanol, ethanol and butanol, and the like.

[0034] Non-restricted examples of the acid anhydride are, for instance, phthalic anhydride, pyromellitic anhydride, mellitic anhydride, and the like.

[0035] The polysilane compound is a compound having two or more groups selected from SiOH group and hydrolyzable group directly bonded to silicon atom or a condensate thereof, and the compounds described, for example, in JP-A-2-232250, JP-A-2-232251, etc. can be used. Examples thereof are dimethyldimethoxysilane, dibutyldimethoxysilane, diisopropyldipropoxysilane, diphenyldibutoxysilane, diphenylethoxysilane, diethyldisilanol, dihexyldisilanol-methyltrimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, propyltrimethoxysilane, phenyltriethoxysilane, phenyltributoxysilane, hexyltriacetoxysilane, methyltrisilanol, phenyltrisilanol, tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, tetraacetoxysilane, diisopropoxydivaleroxysilane, tetrasilanol, and the like.

[0036] Examples of the usable polyepoxy compound and isocyanate group-containing silane compound are, for instance, those described in JP-A-2-232250, JP-A-2-232251, etc. Examples of the suitable compounds are



and the like.

[0037] An adding amount of the curing agent is from 0.1 to 5 equivalents, preferably 0.5 to 1.5 equivalents to 1 equivalent of the reactive curable group in the above-mentioned curable fluorine-containing resin. The coating film can be cured usually at 0° to 200°C for about several seconds to about ten days.

[0038] To the coating composition to be used in the present invention can be added various additives. Examples of the additive are those usually used, such as a curing accelerator, pigment, pigment dispersing agent, dye, leveling agent, defoaming agent, gelation preventing agent, ultraviolet ray absorber, anti-oxidant, plasticizer and thickener.

[0039] Examples of the curing accelerator are, for instance, organotin compounds, alkyl acid phosphates, reaction products of amine with alkyl acid phosphates, saturated or unsaturated polyvalent carboxylic acids or acid anhydrides thereof, organotitanate compounds, amine compounds, lead octylate, and the like.

[0040] The curing accelerators may be used solely or in a mixture of two or more thereof.

[0041] An adding amount of the curing accelerator is preferably from about  $1.0 \times 10^{-6}$  parts by weight to about  $1.0 \times 10^{-2}$  parts by weight, further preferably from about  $5.0 \times 10^{-5}$  parts by weight to about  $1.0 \times 10^{-3}$  parts by weight on the basis of 100 parts by weight of fluorine-containing resin.

[0042] Non-restricted examples of the pigment are, for instance, an inorganic pigment such as titanium oxide, calcium

carbonate or carbon black; an organic pigment such as phthalocyanine, quinacridone or azo pigment; and the like. An adding amount of the pigment is usually up to about 200 % by weight based on the fluorine-containing resin.

[0043] In the present invention, the coating composition can be prepared in the form of organic solvent composition, water dispersible composition and non-water-dispersible dispersion. From the viewpoint of storage stability of dye and curing reactivity, organic solvent composition is preferred.

[0044] In case of the organic solvent composition, examples of the solvent are esters such as ethyl acetate, butyl acetate, isopropyl acetate, isobutyl acetate, cellosolve acetate and propylene glycol methyl ether acetate; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone and cyclohexane; cyclic ethers such as tetrahydrofuran and dioxane; amides such as N,N-dimethylformamide and N,N-dimethylacetamide; aromatic hydrocarbons such as toluene and xylene; alcohols such as propylene glycol methyl ether; hydrocarbons such as hexane and heptane; solvent mixture thereof; and the like. A resin concentration is from 1 to 95 % by weight, preferably 5 to 70 % by weight.

[0045] The leather coated with the fluorine-containing resin coating composition of the present invention can be obtained by applying the above-mentioned curable fluorine-containing resin coating composition to the leather directly or through a primer layer and then carrying out curing.

[0046] For the primer layer, conventional primer resins can be used. For example, the primer layer is formed by applying a coating composition comprising an acrylic resin, methacrylic resin, urethane resin, acrylonitrile resin, butadiene resin, styrene resin, vinyl chloride resin, vinylidene chloride resin, vinyl acetate resin or a mixture of two or more thereof. By forming the primer layer, smoothness and uniformity of appearance can be enhanced. Particularly preferred primer are urethane resin and acrylic resin. A coating amount of the primer layer may be selected optionally in a range of from 1 to 100 g/m<sup>2</sup> depending on application, kind of raw leather and surface condition of the leather.

[0047] A coating amount (solid content) of the cured fluorine-containing coating film which is formed as the outermost layer of the coated leather of the present invention may be optionally selected in a range of not less than 2 g/m<sup>2</sup>.

[0048] A coating method is not limited particularly as far as the above-mentioned coating thickness can be obtained. For example, spray coating, brush coating, curtain coating, roll coating, and the like method can be employed.

[0049] A curing method of a coating film differs depending on kinds of a curing agent and curing accelerator, a coating amount, application of the coated leather, etc. For example, there are (1) a method of allowing to stand at room temperature for five days, (2) a method of allowing to stand at 50°C for two minutes in a hot air drying oven, (3) a method of heating for 10 seconds with an infrared heater, and the like method.

[0050] Kind of a leather to be coated is not limited depending on kind of animal, a processing method, application, etc., and various kinds of leathers can be used. For example, there are leathers of animals such as cow, sheep, goat, pig, horse, kangaroo and deer. Examples of the surface finishing of the leather are full grain leather, corrected grain leather, pasted leather, embossing leather, shrink leather and patent leather.

[0051] The cured fluorine-containing coating film of the present invention is excellent in transparency, and when coating directly or through a transparent primer layer, it is possible to make the best use of a surface pattern of the leather. Also when a primer layer is colored by adding a pigment to the primer or when a pigment is added to the curable fluorine-containing resin coating composition for coloring, a tone of color of the pigment can be made vivid. Thus the leather of the present invention coated with the fluorine-containing resin coating composition is excellent in not only stain-proofing property, solvent resistance, cold resistance and flexing fatigue resistance but also a property for keeping a surface pattern.

[0052] Accordingly the leather of the present invention coated with the fluorine-containing resin coating composition can be processed into various leather products.

[0053] Examples thereof are, for instance, interior of building; interior of vehicles such as seat, head rest, arm rest, steering wheel, inner lining of door and lining of ceiling of automobile, seat and inner lining of aircraft, seat of train and seat of marine vessel; leather-covered furniture such as sofa, chair for living room and chair and table for dining room; shoes made of leather such as boots, pumps, men's shoes, sports shoes and safety shoes; leather bags such as knapsack, handbag, shoulder-strap bag, pouch, traveling bag and rucksack; leather wears such as skirt, overcoat, pants, jacket, motorcyclist's suits, ski suits, gloves and hat; small leather articles such as purse, belt, watch band, pocket notebook, harness and book cover; fabrics for handicraft; and the like. The leather product may be produced by cutting and sewing the coated leather of the present invention or forming into a leather product and then coating.

[0054] Then the leather of the present invention coated with the fluorine-containing coating composition is explained by means of examples, but the present invention is not limited to them. "Part" and "%" represent "part by weight" and "% by weight", respectively.

#### EXAMPLE 1

[0055] A commercially available urethane resin coating for primer of a leather was coated on a white cowhide (chrome-tanned steer hide grain leather) with a spray gun to form a primer layer having a coating amount of 10 g/m<sup>2</sup>. Separately a curable fluorine-containing resin coating composition was prepared by adding 11 parts of CORONATE

HX (hexamethylene diisocyanate curing agent available from NIPPON POLYURETHANE INDUSTRY CO., LTD.) to 100 parts of ZEFFLE GK500 (TFE resin coating composition having hydroxyl group as a reactive curable group and being available from DAIKIN INDUSTRIES, LTD., Hydroxyl value of solid content of resin: 60 mgKOH/g, Acid value: 0 mgKOH/g) (NCO/OH=1) and then dispersing the mixture in 400 parts of butyl acetate.

[0056] The obtained coating composition was coated on the primer layer of white cowhide with a spray gun and cured at 50°C for two minutes to give the leathers of the present invention coated with the fluorine-containing resin coating composition which have an outermost layer of a fluorine-containing resin coating film of 2 g/m<sup>2</sup> and 10 g/m<sup>2</sup> (solid content), respectively.

[0057] With respect to the obtained white leathers coated with the fluorine-containing resin coating composition, the above-mentioned stain removing test, cold resistance test and flexing fatigue resistance test were carried out. The results are shown in Table 1.

[0058] Further the leathers of the present invention coated with the fluorine-containing resin coating composition were obtained in the same manner as in the above-mentioned white cowhide except that a dark blue cowhide (chrome-tanned steer hide grain leather having 10 g/m<sup>2</sup> of urethane resin coating film as a primer layer) was used.

[0059] The above-mentioned ethanol resistance test was carried out by using the dark blue leathers coated with the fluorine-containing resin coating composition. The results are shown in Table 1.

#### EXAMPLES 2 to 13

[0060] White leathers coated with a fluorine-containing resin coating composition and dark blue leathers coated with a fluorine-containing resin coating composition were produced in the same manner as in Example 1 except that a curable fluorine-containing resin and a curing agent were changed to resins shown in Table 2 and mixed in a ratio of NCO/OH=1. A stain removing test, cold resistance test, flexing fatigue resistance test and ethanol resistance test were carried out. The results are shown in Table 2.

[0061] The resins used were as follows

ZEFFLE GK-510: TFE resin coating composition having hydroxyl group available from DAIKIN INDUSTRIES, LTD., hydroxyl value of resin solid content: 60 mgKOH/g, acid value: 9 mgKOH/g

ZEFFLE GK-550: TFE resin coating composition having hydroxyl group available from DAIKIN INDUSTRIES, LTD., hydroxyl value of resin solid content: 95 mgKOH/g, acid value: 0 mgKOH/g

LUMIFLON LF-200: CTFE resin coating composition having hydroxyl group available from ASAHI GLASS CO., LTD., hydroxyl value of resin solid content: 53 mgKOH/g, acid value: 0 mgKOH/g

TAKENATE D-177N: Hexamethylene diisocyanate curing agent available from TAKEDA CHEMICAL INDUSTRIES, LTD.

CORONATE 2094: Hexamethylene diisocyanate curing agent available from NIPPON POLYURETHANE INDUSTRY CO., LTD.

#### COMPARATIVE EXAMPLE 1

[0062] A white leather coated with a urethane resin coating composition and a dark blue leather coated with a urethane resin coating composition for comparison were produced in the same manner as in Example 1 except that a commercially available non-fluorine-containing urethane resin coating composition for finishing of a leather was used instead of the fluorine-containing resin coating composition. A stain removing test, cold resistance test, flexing fatigue resistance test and ethanol resistance test were carried out. The results are shown in Table 1.

#### COMPARATIVE EXAMPLES 2 and 3

[0063] A white leather coated with a fluorine-containing resin coating composition and a dark blue leather coated with a fluorine-containing resin coating composition were produced in the same manner as in Example 1 except that a curable fluorine-containing resin, a curing agent, a mixing ratio thereof and coating amount were changed as shown in Table 2, and tests were carried out. The results are shown in Table 2.

TABLE 1

| Coating composition of outermost layer                                     | Example 1                                    |                               |   |       | Comparative Example 1 |       |
|--|--|-------------------------------|---|-------|-----------------------|-------|
|  | Fluorine-containing resin<br>(ZEFFLE GK-500) | Curing agent<br>(CORONATE HX) | Commercially available<br>urethane resin coating<br>composition for finishing<br>of leather |       |                       |       |
| Coating amount (g/m <sup>2</sup> , solid content)                          | 2  | 10                            | 2   | 10    | 2                     | 10    |
| Stain removing test  |  |                               |   |       |                       |       |
| Rouge/detergent  | 4 - 5  | 5                             | 3 - 4   | 3 - 4 | 3 - 4                 | 3 - 4 |
| Rouge/cleaner for leather  | 4 - 5  | 5                             | 3   | 3 - 4 | 3 - 4                 | 3 - 4 |
| Mustard/detergent  | 4  | 5                             | 3 - 4   | 3 - 4 | 3 - 4                 | 3 - 4 |
| Mustard/cleaner for leather  | 4 - 5  | 5                             | 3 - 4   | 3 - 4 | 3 - 4                 | 3 - 4 |
| Ink of ball-point pen/detergent  | 4  | 4                             | 3   | 3     | 3                     | 3     |
| Ink of ball-point pen/ cleaner for leather                                 | 5  | 5                             | 3 - 4   | 3 - 4 | 3 - 4                 | 3 - 4 |
| Ethanol resistance test (area percentage % of<br>coating film chipped off) | 50   | 0                             | 100   | 90    | 90                    | 90    |
| Cold resistance test (Cracking of coating film)                            | Nil  | Nil                           | Nil   | Nil   | Nil                   | Nil   |
| Flexing fatigue resistance test (Cracking of<br>coating film)              | Nil  | Nil                           | Nil   | Nil   | Nil                   | Nil   |



TABLE 2

|   | Example         |               |                 |               |                 |                 |  |
|---|-----------------|---------------|-----------------|---------------|-----------------|-----------------|--|
|   | 2               | 3             | 4               | 5             | 6               | 7               |  |
| Fluorine-containing resin used  | ZEFFLE GK-510   | ZEFFLE GK-510 | ZEFFLE GK-550   | ZEFFLE GK-550 | LUMIFLON LF-200 | LUMIFLON LF-200 |  |
| Curing agent used   | TAKENATE D-177N | CORONATE 2094 | TAKENATE D-177N | CORONATE 2094 | TAKENATE D-177N | CORONATE 2094   |  |
| Mixing ratio  |                 |               |                 |               |                 |                 |  |
| Equivalent (NCO/OH)   | 1               | 1             | 1               | 1             | 1               | 1               |  |
| Coating amount (g/m <sup>2</sup> , solid content)                       | 2               | 2             | 2               | 2             | 2               | 2               |  |
| Stain removing test   |                 |               |                 |               |                 |                 |  |
| Rouge/detergent   | 4 - 5           | 4 - 5         | 4 - 5           | 4 - 5         | 4 - 5           | 4 - 5           |  |
| Ink of ball-point pen/cleaner for leather                               | 5               | 4 - 5         | 4 - 5           | 4 - 5         | 4 - 5           | 4               |  |
| Ethanol resistance test (area percentage % of coating film chipped off) | 25              | 25            | 25              | 25            | 50              | 50              |  |
| Cold resistance test (Cracking of coating film)                         | Nil             | Nil           | Nil             | Nil           | Nil             | Nil             |  |
| Flexing fatigue resistance test (Cracking of coating film)              | Nil             | Nil           | Nil             | Nil           | Nil             | Nil             |  |

- continued -

- continued -

| Example            |                  |                    |                  | Comparative Example |                    |                  |                      |
|--------------------|------------------|--------------------|------------------|---------------------|--------------------|------------------|----------------------|
| 8                  | 9                | 10                 | 11               | 12                  | 13                 | 2                | 3                    |
| ZEFFLE<br>GK-510   | ZEFFLE<br>GK-510 | ZEFFLE<br>GK-550   | ZEFFLE<br>GK-550 | LUMIFLON<br>LF-200  | LUMIFLON<br>LF-200 | ZEFFLE<br>GK-510 | ZEFFLE<br>GK-550     |
| TAKENATE<br>D-177N | CORONATE<br>2094 | TAKENATE<br>D-177N | CORONATE<br>2094 | TAKENATE<br>D-177N  | CORONATE<br>2094   | CORONATE<br>2094 | TAKENATE<br>D-177N   |
| 1                  | 1                | 1                  | 1                | 1                   | 1                  | 1                | 10                   |
| 10                 | 10               | 10                 | 10               | 10                  | 10                 | 0.5              | 10                   |
| 5                  | 5                | 5                  | 5                | 5                   | 5                  | 3 - 4            | 4                    |
| 5                  | 4 - 5            | 5                  | 4 - 5            | 4 - 5               | 4 - 5              | 3 - 4            | 4                    |
| 0                  | 0                | 0                  | 0                | 0                   | 10                 | 75               | 50                   |
| Nil                | Nil              | Nil                | Nil              | Nil                 | Nil                | Nil              | Cracking<br>occurred |
| Nil                | Nil              | Nil                | Nil              | Nil                 | Nil                | Nil              | Cracking<br>occurred |

[0064] As it is clear from Tables 1 and 2, stain removability against various stains are enhanced with respect to the leather coated with the fluorine-containing resin coating composition of the present invention.

[0065] Also cold resistance and flexing fatigue resistance are maintained, and solvent resistance is improved.

## 5 INDUSTRIAL APPLICABILITY

[0066] According to the present invention, by forming the outermost layer of the coated leather with a curable fluorine-containing resin, stain removability and solvent (ethanol) resistance are enhanced, and cold resistance and flexing fatigue resistance, lowering of which was cared by the use of fluorine-containing resin, can be maintained at a level of conventional urethane resin coating.

## Claims

- 15 1. A leather coated with a fluorine-containing resin coating composition, which has an outermost layer of a fluorine-containing resin coating film, in which in stain removing test according to JIS L 0805, a grey scale is grade 4 or more and in ethanol resistance test according to JIS K 6547 by using a clock meter type friction tester, an area of chipped-off fluorine-containing coating film is 50 % or less.
- 20 2. The leather coated with a fluorine-containing resin coating composition of Claim 1, wherein in said stain removing test, a stain is marked with a rouge, the stain is allowed to stand for 30 minutes and a neutral detergent is used as a stain removing agent.
- 25 3. The leather coated with a fluorine-containing resin coating composition of Claim 1, wherein in the cold resistance test in which the leather is allowed to stand at -5°C for 24 hours and folded with its coated surface being faced outward, a cracking does not arise on the fluorine-containing resin coating film.
- 30 4. The leather coated with a fluorine-containing resin coating composition of any of Claims 1 to 3, wherein in a flexing fatigue resistance test which is carried out by bending the coated leather 30,000 times by using a flexometer described in JIS K 6545, a cracking does not arise on the fluorine-containing resin coating film.
5. The leather coated with a fluorine-containing resin coating composition of any of Claims 1 to 4, which has the fluorine-containing resin coating film of 2 g/m<sup>2</sup>.
- 35 6. The leather coated with a fluorine-containing resin coating composition of any of Claims 1 to 5, wherein the fluorine-containing resin coating film is formed by curing a curable fluorine-containing resin coating composition comprising a fluorine-containing resin having a reactive curable group and a curing agent.
- 40 7. The leather coated with a fluorine-containing resin coating composition of Claim 6, wherein the reactive curable group is at least one of hydroxyl group, amino group, epoxy group, carboxyl group, mercapto group, hydrolyzable silyl group, amido bond, urethane bond and urea bond.
8. The leather coated with a fluorine-containing resin coating composition of Claim 6, wherein the reactive curable group is hydroxyl group.
- 45 9. The leather coated with a fluorine-containing resin coating composition of Claim 8, wherein a hydroxyl value of the fluorine-containing resin having hydroxyl group is not more than 200 mgKOH/g.
- 50 10. The leather coated with a fluorine-containing resin coating composition of any of Claims 6 to 9, wherein the fluorine-containing resin is a polymer having at least one of chlorotrifluoroethylene unit, tetrafluoroethylene unit, trifluoroethylene unit, hexafluoropropylene unit, vinylidene fluoride unit and vinyl fluoride unit.
- 55 11. The leather coated with a fluorine-containing resin coating composition of any of Claims 6 to 10, wherein the curing agent is an isocyanate compound, amino resin, acid anhydride, polysilane compound, polyepoxy compound or silane compound having isocyanate group.
12. The leather coated with a fluorine-containing resin coating composition of any of Claims 1 to 11, wherein the fluorine-containing resin coating film is formed directly on the leather.

13. The leather coated with a fluorine-containing resin coating composition of any of Claims 1 to 11, wherein a primer layer is formed between the leather and the fluorine-containing resin coating film.
14. The leather coated with a fluorine-containing resin coating composition of Claim 13, wherein the primer layer is a non-fluorine-containing coating film comprising an acrylic resin, methacrylic resin, urethane resin, acrylonitrile resin, butadiene resin, styrene resin, vinyl chloride resin, vinylidene chloride resin, vinyl acetate resin or a mixture of two or more thereof.
15. A method of producing the leather coated with the fluorine-containing resin coating composition of any of Claims 1 to 5, which comprises coating the curable fluorine-containing resin coating composition of any of Claims 6 to 11 on the leather surface directly or through a primer layer, and curing.
16. The production method of Claim 15, wherein the fluorine-containing resin coating composition is coated on the leather directly without forming a primer layer between the leather and the coating film of the resin coating composition.
17. The production method of Claim 15, wherein the fluorine-containing resin coating composition is coated after coating the primer layer on the leather.
18. The production method of Claim 17, wherein the primer layer is the non-fluorine-containing coating film of Claim 14.
19. The leather coated with a fluorine-containing resin coating composition of any of Claims 1 to 14, which is used for interior goods of building, interior goods of vehicles, furniture, shoes, bags, clothes and small leather articles.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/03914

| A. CLASSIFICATION OF SUBJECT MATTER<br>Int. Cl. <sup>6</sup> C14C11/00  |  |   |
|---|--|---|
| According to International Patent Classification (IPC) or to both national classification and IPC   |  |   |
| B. FIELDS SEARCHED  |  |   |
| Minimum documentation searched (classification system followed by classification symbols)<br>Int. Cl. <sup>6</sup> C14C9/00-11/00   |  |   |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched<br>Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1999<br>Kokai Jitsuyo Shinan Koho 1971-1999 Jitsuyo Shinan Toroku Koho 1996-1999   |  |   |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  |  |   |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT  |  |   |
| Category*   | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No.   |
| Y   | JP, 8-113800, A (Du Pont K.K.),<br>7 May, 1996 (07. 05. 96),<br>Refer to page 1, abstract, object, constitution ;<br>page 3, Par. Nos. [0011], [0012] (Family: none)   | 1-4, 12-14  |
| A   | JP, 8-113800, A (Du Pont K.K.),<br>7 May, 1996 (07. 05. 96) (Family: none)   | 5-11, 15-18   |
| A   | JP, 3-174418, A (Bayer AG.),<br>29 July, 1991 (29. 07. 91)<br>& DE, 3935859, A1 & EP, 424765, A2<br>& US, 5093398, A & EP, 424765, B1  | 1-19  |
| A   | JP, 3-218349, A (Atochem),<br>25 September, 1991 (25. 09. 91)<br>& FI, 905431, A0 & NO, 904780, A0<br>& FR, 2653772, A1 & AU, 6579590, A1<br>& KR, 9307500, B1 & EP, 426530, B1<br>& AT, 107668, E & DE, 69010145, C0<br>& ES, 2055885, T3 | 1-19  |
| <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.  |  |   |
| * Special categories of cited documents:<br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"E" earlier document but published on or after the international filing date<br>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed<br>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone<br>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art<br>"&" document member of the same patent family |  |   |
| Date of the actual completion of the international search<br>19 October, 1999 (19. 10. 99)  |  | Date of mailing of the international search report<br>26 October, 1999 (26. 10. 99) |
| Name and mailing address of the ISA/<br>Japanese Patent Office  |  | Authorized officer  |
| Facsimile No.   |  | Telephone No.   |

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/03914

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |   |                       |
|---|---|-----------------------|
| Category*   | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
| A   | JP, 48-23901, A (Bayer AG.),<br>28 March, 1973 (28. 03. 73) (Family: none)  | 1-19                  |
| Y   | JP, 8-113800, A (Du Pont K.K.),<br>7 May, 1996 (07. 05. 96),<br>Refer to page 2, Par. No. [0002], "Prior Art"<br>(Family: none) | 19                    |

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